



## Research paper

## Graphene quantum dots modified mesoporous graphite carbon nitride with significant enhancement of photocatalytic activity



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## ABSTRACT

Hydroxyl-graphene quantum dots (GQDs) modified mesoporous graphitic carbon nitride (mpg-C<sub>3</sub>N<sub>4</sub>) composites were fabricated through electrostatic interactions. A variety of techniques were applied to discuss systematic effect on the morphology, optical, electronic properties and structure of GQDs/mpg-C<sub>3</sub>N<sub>4</sub> composites. Remarkably, the 0.5 wt% GQDs/mpg-C<sub>3</sub>N<sub>4</sub> composites exhibited higher photocatalytic activity than that of the pure mpg-C<sub>3</sub>N<sub>4</sub> by using rhodamine B (RhB) and colorless tetracycline hydrochloride (TC) as pollutants under visible light irradiation. The results indicated that uniform dispersion of GQDs on the surface of mpg-C<sub>3</sub>N<sub>4</sub> and intimate contact between the two materials contributed to the enhanced activity. Radical trapping experiments and electron spin resonance tests both certified that the GQDs/mpg-C<sub>3</sub>N<sub>4</sub> composites can generate more •O<sub>2</sub><sup>−</sup> species and a small fraction of holes for photocatalytic degradation.

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## 1. Introduction

The ever growing energy crisis has led to repaid increase in research and development in energy conversion and storage field. However, along with that it has also increased the hazardous impacts on environment. Hence a considerable amount of attention has been shifted toward lowering catastrophic impacts on environment, photocatalysis being one. For the organic pollutants contaminating the water bodies photocatalysis are highly effective. Developing of new visible-light active photocatalysts with abundant, stable materials showing efficient, high activity performance is a key point [1,2]. As a novel class of carbon nitride, melon-based graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is a fascinating  $\pi$ -conjugated semiconductor with suitable electronic structure (band gap = 2.7 eV) [3–6]. Also low cost, easy availability, high stability, non-toxic as well as easily tailor-able structure make g-C<sub>3</sub>N<sub>4</sub> a promising candidate in photocatalytic application [7–11]. Nevertheless, a small specific surface area leading to the rapid recombination of photoinduced electron-holes pairs and insufficient solar-light absorption, inhibit it's further practical

applications. Among the approaches reported emphasis is given to synthesize the modified g-C<sub>3</sub>N<sub>4</sub> photocatalysts [12,13], including doping with nonmetal and metals species, like B, F [14], K [15], Br [16], I [17], P [18], Fe [19] and Au [20]. In addition, fabrication of g-C<sub>3</sub>N<sub>4</sub>-based heterojunction with secondary semiconductors or co-catalysts is also used to increase migration of photo-generated electron [21–25]. The other approach is to fabricate different morphologies g-C<sub>3</sub>N<sub>4</sub> nanospheres [24,26], nanosheets [27–30], nanotubes [31], nanorods [32], helical [33] or seaweed [34] rendering enlarged specific surface area for enhanced photocatalytic activity.

Mesoporous materials are more attractive due to the outstanding properties and potential applications. Mesoporous TiO<sub>2</sub> [35], Co<sub>3</sub>O<sub>4</sub> [36,37] and WO<sub>3</sub> [38] have exhibited well properties in the field of fuel cells, lithium ion batteries, supercapacitor, photocatalytic degradation of organic pollutions, gas storage and separation and dye sensitized solar cells [39–43]. Especially, non-metal nanomaterials, like carbonaceous and carbon nitride nanomaterials, with highly stable and less expensive earth-abundant elements have attracted much attention. Graphitic carbon nitride with mesoporous structure is beneficial to increase the photocatalytic performance due to the enhancing the light harvesting ability and the adsorption capability [44]. Meanwhile, based on the pore structure, it is crucial to further boost the photocatalytic activity of

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pure mpg- $C_3N_4$  by combining a small amount of metal and non-metal oxide, including  $Co_3O_4$ /mpg- $C_3N_4$  [45],  $ZnO$ /mpg- $C_3N_4$  [46],  $TiO_2$ /mpg- $C_3N_4$  [47],  $PW_{12}$ /mpg- $C_3N_4$  [48] and  $WO_3$ /mpg- $C_3N_4$  [49]. These composites have been demonstrated to be capable of remarkably enhancing the photocatalytic activity. However, the object of research in carbon nitride material is to further explore co-catalysts as less expensive and stable performance. Therefore, carbonaceous is no doubt becoming as one of the most popular materials, like graphene, graphene oxide, carbon nanotubes and novel graphene quantum dot materials. Graphene quantum dots (GQDs), as a family of quantum dots materials, has currently aroused increasing attention [50–57]. GQDs with edge-enriched and small size usually possess unique character compared to other carbon materials [58–62].

Herein, we designed GQDs/mpg- $C_3N_4$  materials via a facile approach to solve the limitation of pristine mpg- $C_3N_4$ . The as-prepared GQDs/mpg- $C_3N_4$  composites were obtained through electrostatic attraction between mpg- $C_3N_4$  and GQDs in ethanol solution. To the best of our knowledge, there is no report on the fabrication strategy of GQDs/mpg- $C_3N_4$  by electrostatic attraction. In this study, the electrostatic interaction is as a promising method to solve problem of aggregation and contact. The morphology, structure and optical/electric properties of GQDs/mpg- $C_3N_4$  were evaluated by various physicochemical techniques. The results indicated that the GQDs/mpg- $C_3N_4$  composites exhibited much higher visible-light performance than pristine mpg- $C_3N_4$  due to the incorporation of GQDs.

## 2. Experimental section

### 2.1. Preparation of photocatalysts

All chemicals were of analytically grade. The GQDs were synthesized according to the papers through an alkali-catalyzed water-phase molecular fusion method [63].

#### 2.1.1 Preparation of OH-functionalized GQDs

Hydroxyl-functionalized GQDs were synthesized according to our previous work [63,64]. In this synthesis procedure, 2 g pyrene was nitrated into trinitropyrene in hot  $HNO_3$  at 80 °C under refluxing and stirring for 12 h. After cooled to room temperature, the mixture was dissolved in distilled water and filtered through a 0.22  $\mu m$  microporous membrane to remove to acid. The resultant yellow trinitropyrene was dispersed in 0.2 M NaOH by ultrasonication for 2 h. The suspension was transferred to a 100 mL Teflon-lined stainless steel autoclave for 10 h at 200 °C. After cooling, the water-soluble GQDs were obtained through 0.22  $\mu m$  microporous membrane to remove impurities (insoluble carbon products). The purified black GQDs were dissolved in distilled water.

#### 2.1.2 Preparation of mpg- $C_3N_4$

The pure mpg- $C_3N_4$  was synthesized using  $SiO_2$  as hard template [65–67]. Firstly, cyanamide was added in silica colloidal solution (mass ratios, cyanamide: template = 0.5). The mixture solution was stirred at room temperature for 4 h and heated at 60 °C for 2 h to get transparent gel. The resulting gel was heated to 550 °C in  $N_2$  flow at a rate of 2.3 °C/min, dwelling for 4 h. The silica template was removed by  $NH_4HF_2$ . The sample was separated by centrifuging, washing with ultrapure water and ethanol.

#### 2.1.3 Synthesis of GQDs/mpg- $C_3N_4$ composites

The GQDs/mpg- $C_3N_4$  composites were synthesized as follows. Firstly, an appropriate amount of mpg- $C_3N_4$  was dissolved into 15 mL ethanol and sonicated for 30 min to obtain a homogeneous suspension. Then, a certain concentration GQDs solution

was dispersed in the above solution and stirred for 12 h. After ethanol vaporization, the powder was obtained after drying at 80 °C. GQDs/mpg- $C_3N_4$  photocatalysts with different GQDs content designated as X wt% GQDs/mpg- $C_3N_4$ , wherein "X" represent the mass percentage of GQDs (X = 0.1, 0.2, 0.5, 1, 2 and 3 wt%).

### 2.2. Characterization of materials

The crystal structures of photocatalysts were recorded by X-ray diffraction (XRD) using Shimadzu XRD-6000 with  $Cu K\alpha$  radiation in the range of 2 $\theta$  from 10° to 80°. The chemical environment of as-prepared photocatalysts were analyzed by X-ray photoelectron spectroscopy (XPS) using VG MultiLab 2000 system with a monochromatic  $Mg-K\alpha$  source operated at 20 kV. The nitrogen adsorption-desorption isotherms (TriStar II 3020) was used to calculate surface area and pore size of as-prepared samples in the relative pressure range of 0.1–0.9. Transmission electron microscopy (TEM) images of all samples were performed on JEOL JEM-2010 (200 kV). The Z-potential was carried out on the Malvern Zetasizer Nano-S90 (England). Diffuse reflection spectra (DRS) was acquired on Shimadzu UV-2450 spectrophotometer in the range of 200–800 nm ( $BaSO_4$  as reference material). Composition analysis of as-prepared materials were carried on the Fourier transforms infrared spectra (FT-IR) using Nicolet Nexus 470 spectroscopy. The photoluminescence spectra of as-prepared materials were monitored on a QuantaMaster & TimeMaster Spectrofluorometer (excitation wavelength at 360 nm). Electron spin resonance (ESR) spectra was conducted on a Bruker model ESR JES-FA200 spectrometer.

### 2.3. Photocatalytic activity measurements

The photocatalytic performance of GQDs/mpg- $C_3N_4$  samples was investigated using 10 mg/L RhB and 20 mg/L TC as pollutants. 25 mg and 50 mg GQDs/mpg- $C_3N_4$  composites were dispersed in the Pyrex photocatalytic reactors including 50 mL RhB dye and colorless TC, respectively. Photocatalytic reaction apparatus with 300 W Xe arc lamp was used as light source with a filter ( $\lambda > 400$  nm) to provide the visible light. The photocatalytic experiments were performed at constant temperature by a circulating water system. Prior to light irradiation, the suspension was stirred for 30 min without light to reach adsorption and desorption equilibrium, and this adsorption equilibrium point is the starting point of photocatalytic reaction. During the photoreaction process, 3 mL suspension was collected at 30 min intervals and centrifuged. The decay of absorbance of organic dye RhB and TC were analyzed by an UV-vis spectrophotometer at wavelength 553 nm and 356 nm, respectively.

### 2.4. Photoelectrochemical measurements

Photocurrent measurements were carried out a CHI 660B electrochemical workstation (Chenhua Instrument), including a standard three electrodes system configuration with a platinum wire as counter electrode, an  $Ag/AgCl$  wire (saturated KCl solution) as reference electrode, and 0.1 M  $Na_2SO_4$  solution as the electrolyte. The working electrode was prepared as followed: 5 mg of sample was dispersed in 1 mL ethylene glycol solution. The suspension was then spread on a 3 cm × 1 cm ITO glass substrate with an active area of about 0.5 cm × 1 cm and dried under infrared lamp to form mpg- $C_3N_4$  and GQDs/mpg- $C_3N_4$  modified ITO electrodes. 500 W Xe lamp was used as light source.

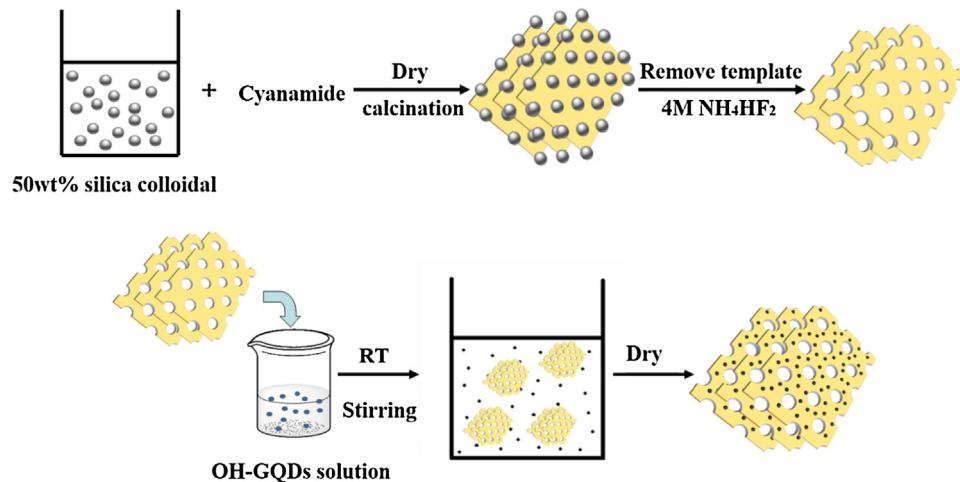


Fig. 1. Schematic for the synthesis process of GQDs/mpg- $C_3N_4$  by electrostatic attraction.

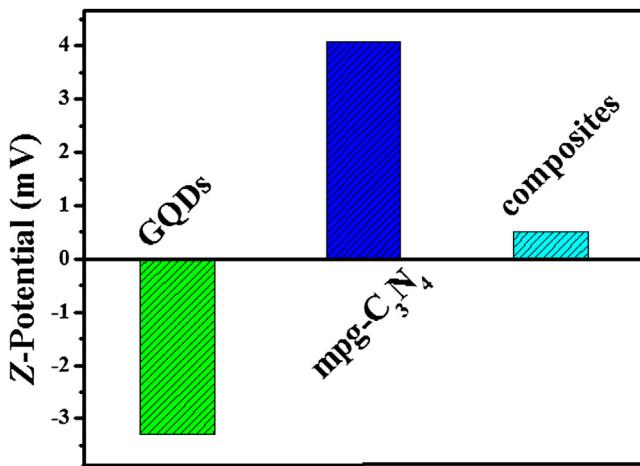


Fig. 2. Z-potential of mpg- $C_3N_4$ , GQDs and GQDs/mpg- $C_3N_4$  in ethanol solution.

### 3. Results and discussion

#### 3.1. The proposed formation process of GQD/mpg- $C_3N_4$

For the synthesis of GQDs/mpg- $C_3N_4$  with different mass ratios, a general electrostatic interactions method was introduced to fabricate a homogeneous solution, as shown in Fig. 1. To investigate the formation process of composites, electrostatic attraction of two materials was tested by the Z-potential apparatus and the results were shown in Fig. 2. Z-potential of mpg- $C_3N_4$  was 4.07 mV due to the use of  $NH_4HF_2$  as etchant, indicating that etching process rendered mpg- $C_3N_4$  positive charge on surface. In comparison to mpg- $C_3N_4$ , Z-potential of GQDs was -3.28 mV, suggesting negative polarity. Therefore, the spontaneous assembly between the negatively charged GQDs and the positively charged mpg- $C_3N_4$  was achieved. The Z-potential of the GQDs/mpg- $C_3N_4$  was decreased to 0.5 eV, indicating that GQDs successfully adsorbed on the surface of multilayer mpg- $C_3N_4$  sheets. Owing to electrostatic attraction between mpg- $C_3N_4$  and GQDs, it is beneficial for the homogenous dispersion of GQDs. The above results are further confirmed by TEM investigation. As shown in Fig. 3a, the TEM images of GQDs exhibited uniformly size about 5 nm. The Fig. 3b shows that the GQDs are well dispersed with uniform lateral sizes. The average size of GQDs determined by TEM is about 5 nm. The Fast Fourier Transformation (FFT) pattern show that the GQDs are almost defect-free graphene single crystals (Fig. 3c). Many spherical pores with a mean diameter of about 20 nm were observed on the surface of the mpg- $C_3N_4$  (Fig. 3d and e), suggesting that the holes of mpg- $C_3N_4$  successfully copied by HS-40 colloidal solution. After introduction of the GQDs into mpg- $C_3N_4$ , 0.5 wt% GQDs/mpg- $C_3N_4$  composites have the similar porosity structure comparison to the pure mpg- $C_3N_4$  (Fig. 3f). Meanwhile, the GQDs easily combine with mpg- $C_3N_4$  and disperse well via electrostatic attraction [68,69].

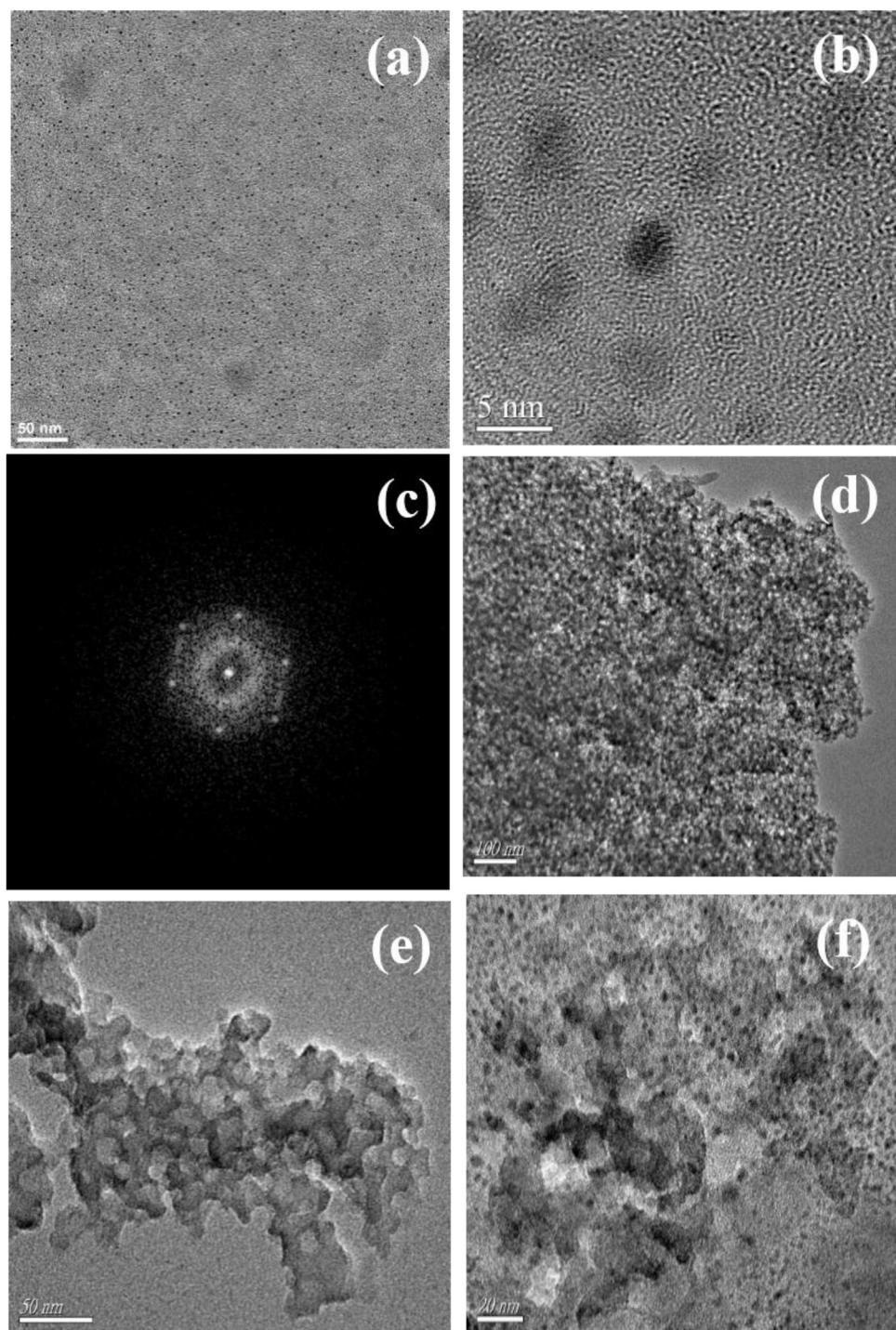
Fig. 1. Schematic for the synthesis process of GQDs/mpg- $C_3N_4$  by electrostatic attraction.

#### 3.2. XRD and FT-IR analysis

The structural characteristics of as-prepared mpg- $C_3N_4$  and GQDs/mpg- $C_3N_4$  with the different mass ratios of GQDs were measured by XRD technique (Fig. 4a). The pure mpg- $C_3N_4$  displays two distinct diffraction peaks at  $13.0^\circ$  (100) reflection and  $27.4^\circ$  (002), which indicated the characteristic graphitic-like layered stacking of CN-based materials. Nevertheless, there was no characteristic peak attributed to GQDs, which may due to the low GQDs content and high dispersion in as-prepared GQDs/mpg- $C_3N_4$  composites. It also found that the GQDs modification has no significant effect on the layer-shaped structure of mpg- $C_3N_4$ . Fig. 4b presents FT-IR spectra of GQDs/mpg- $C_3N_4$  samples. The pure mpg- $C_3N_4$  exhibited characteristic FT-IR peaks similar to the previous reports [48]. The peaks from  $3000$  to  $3600\text{ cm}^{-1}$  are assigned to N–H groups originated from the incomplete condensation or the residual hydrogen atoms bound to the edges of the graphite-like CN. The s-triazine ring mode at  $808\text{ cm}^{-1}$  and stretching vibration modes in the regions of  $1200$ – $1650\text{ cm}^{-1}$  belongs to C=N and C–N heterocycles. However, the characteristic signal C–OH of OH-GQDs at  $1270\text{ cm}^{-1}$  not detected in the FT-IR spectrum, which is mainly due to strong stretching vibration of C–N.

#### 3.3. XPS analysis

XPS is employed to determine the chemical states and characterize the intimate interaction between GQDs and mpg- $C_3N_4$ . Fig. 5a shows the survey XPS spectra of pure mpg- $C_3N_4$  and 0.5 wt% GQDs/mpg- $C_3N_4$ , indicating the presence of carbon, nitrogen and oxygen. In Fig. 5b, high-resolution C 1s spectra of pure mpg- $C_3N_4$  can be de-convoluted into two species: C=C (284.6 eV) and  $sp^2$ -hybridized carbon in N=C–N<sub>2</sub>= (288.2 eV), whereas the peak of GQDs/mpg- $C_3N_4$  at 285.9 eV is assigned to C–OH of GQDs [70], demonstrating the co-existence of GQDs and mpg- $C_3N_4$  in the composites attributed to spontaneous self-assembly between GQDs and mpg- $C_3N_4$ . Fig. 5c presents high-resolution N 1s spectrum with four species peaks at 398.7 eV, 399.8 eV, 401.0 eV and 404.4 eV,



**Fig. 3.** TEM images (a, b) and Fast Fourier Transformation (FFT) pattern (c) of GQDs; TEM images of the pure mpg- $C_3N_4$  (d, e) and 0.5 wt% GQDs/mpg- $C_3N_4$  composites (f).

respectively. The signal peak at 398.7 eV is attributed to electrons originated from  $sp^2$ -hybridized nitrogen atoms in  $C=N-C$ , which is in good agreement the FT-IR analysis. While two main peaks at 399.8 eV and 401.0 eV are attributed to the tertiary nitrogen ( $N-(C_3)$ ) and the amino functions carrying hydrogen ( $C-N-H$ ) of pure mpg- $C_3N_4$ , which correspond to structural defects and incomplete condensation in the process of cyanamide polycondensation. The weak peak at 404.4 eV may be assigned to  $\pi$ -excitation. From the high-resolution XPS spectrum of O 1s (Fig. 5d), the peak of pure mpg- $C_3N_4$  at 531.3 eV is assigned to O-H, while appear a new peak at 533.2 eV for GQD/mpg- $C_3N_4$  sample, revealing the presence of

C-OH. All above results further confirmed the formation of samples composed of mpg- $C_3N_4$  and GQDs, suggesting the GQDs have been introduced into the multilayer mpg- $C_3N_4$  sheets successfully.

#### 3.4. BET and BJH analysis

The nitrogen adsorption-desorption isotherms of 0.5 wt% GQDs/mpg- $C_3N_4$  and mpg- $C_3N_4$  are shown in Fig. 6. For the pure mpg- $C_3N_4$ , the physical adsorption isotherms show a typical IV with a distinct H1 hysteresis loop observed in the range of  $0.6-1.0 P/P_0$ , which is characteristic of mesoporous structure.

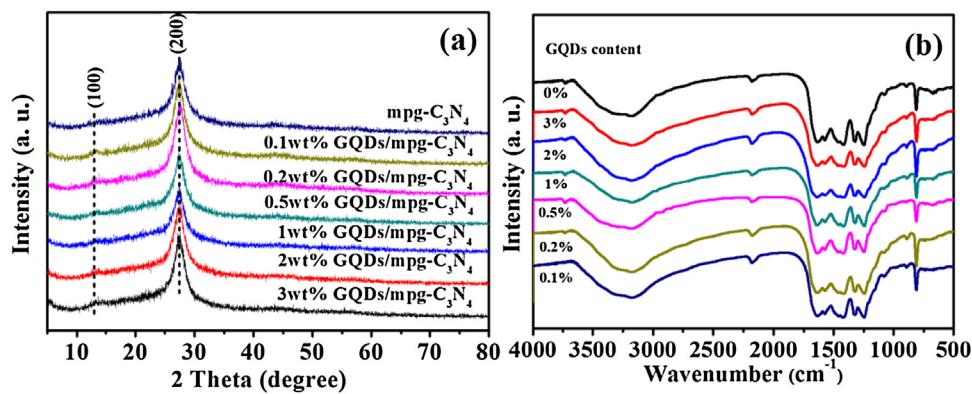


Fig. 4. XRD (a) and FT-IR (b) patterns of mpg-C<sub>3</sub>N<sub>4</sub> and GQDs/mpg-C<sub>3</sub>N<sub>4</sub> with different contents of GQDs.

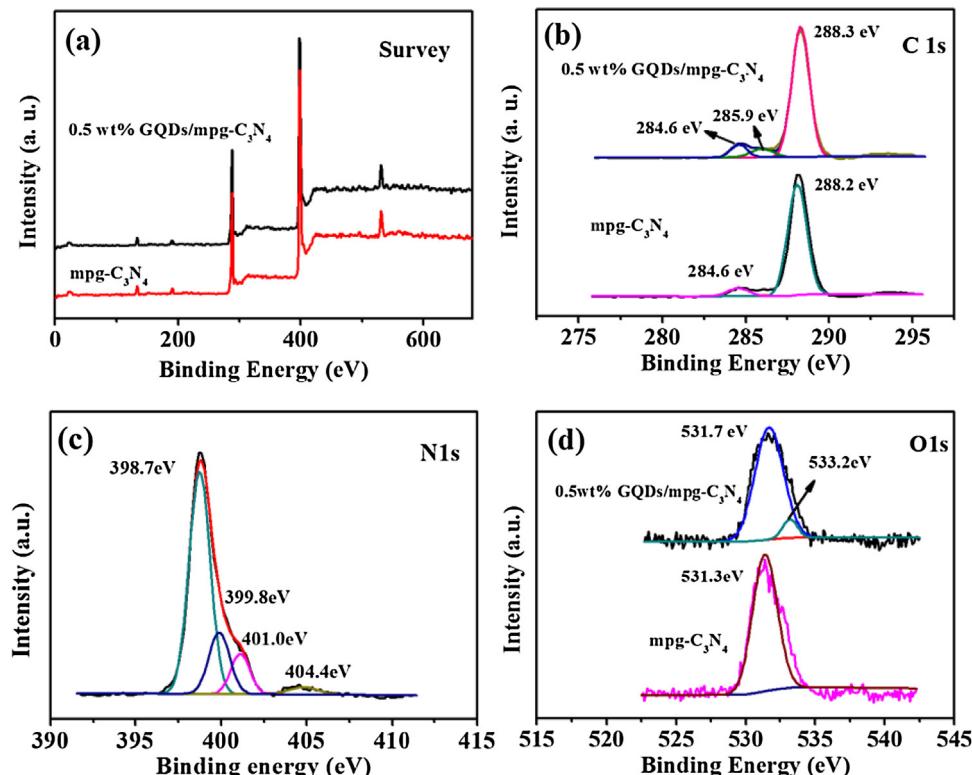


Fig. 5. XPS spectra of mpg-C<sub>3</sub>N<sub>4</sub> and 0.5 wt% GQDs/mpg-C<sub>3</sub>N<sub>4</sub> sample, survey spectrum (a), C 1s (b), N 1s (c) and O 1s (d).

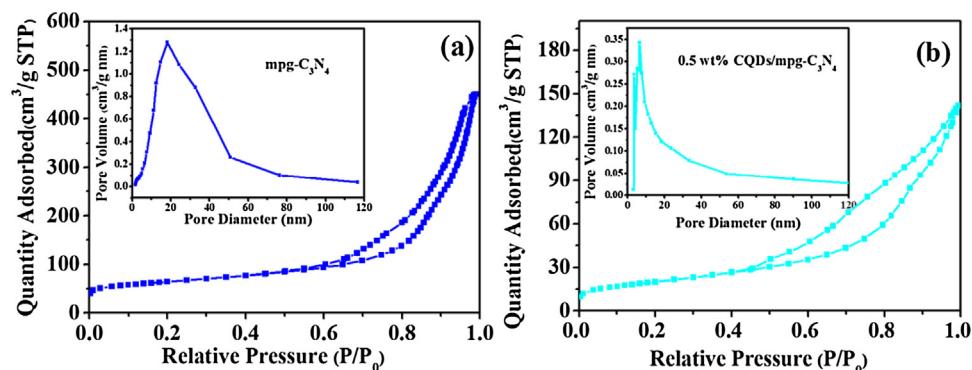


Fig. 6. N<sub>2</sub> adsorption-desorption isotherms and the corresponding pore size distribution curves of pure mpg-C<sub>3</sub>N<sub>4</sub> (a) and 0.5 wt% GQDs/mpg-C<sub>3</sub>N<sub>4</sub> (b).

After the modification of GQDs, the surface area of composites decreased quickly. The specific surface area of pure mpg- $C_3N_4$  is  $158.07\text{ m}^2\text{ g}^{-1}$ , which was larger than that of 0.5 wt% GQDs/mpg- $C_3N_4$  ( $71.3\text{ m}^2\text{ g}^{-1}$ ). However, the mesoporous structure of 0.5 wt% GQDs/mpg- $C_3N_4$  samples still maintained IV type isotherm featuring H1 hysteresis loop at  $0.5\text{--}1.0 P/P_0$ , suggesting that mpg- $C_3N_4$  structure did not damage after incorporating GQDs (Fig. 6b). As shown in Fig. 6a, the appreciable expansion of pore sizes (compared to 12 nm silica template) is found after the replication [71], which may be due to partial hole-wall collapse during the removal of  $\text{SiO}_2$  template. It should be noted that the surface area and average pore size of GQDs/mpg- $C_3N_4$  decreased comparing to pure mpg- $C_3N_4$ , which is mainly due to a part of GQDs blocking the holes of mpg- $C_3N_4$  [72,73]. As far as we know, the larger surface area is favorable to photocatalytic activity, which is mainly attributed to provide more active sites and adsorb more contaminants on the surface of the photocatalyst.

### 3.5. Optical and electronic properties

Fig. 7 shows the effect of GQDs on the absorption spectrum of GQDs/mpg- $C_3N_4$  composites. The pure mpg- $C_3N_4$  exhibits a fundamental absorption edge at 470 nm. It can be found that mpg- $C_3N_4$  alone exhibits almost no absorption in the visible region of 470–800 nm. Nevertheless, the light harvesting capability of GQDs/mpg- $C_3N_4$  composites within the 450 nm to 800 nm gradually improved after modification of GQDs, and thus further to increase photo-generated electron-holes under visible light irradiation, which may be also beneficial to the enhancement of photocatalytic activity.

Photoluminescence techniques are applied to investigate the photo-generated electron-transfer and recombination processes of photo-induced electrons and holes pairs in GQDs, mpg- $C_3N_4$  and GQDs/mpg- $C_3N_4$  samples. The PL peak of GQDs at 525 nm can be

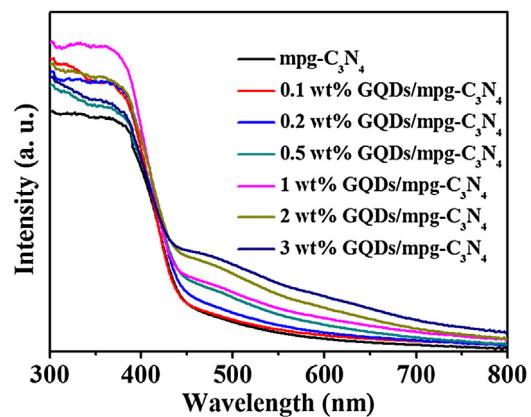


Fig. 7. UV-vis diffuse-reflectance spectra of all samples.

excited in a wide wavelength range (PL, PLE in Fig. 8a). Fig. 8b shows the steady-state PL spectra of the pure mpg- $C_3N_4$  and GQDs/mpg- $C_3N_4$ . As shown in Fig. 8b, pure mpg- $C_3N_4$  (excited at 360 nm) has a strong emission peak centered at about 467 nm. After the modification of GQDs, the emission intensity of GQDs/mpg- $C_3N_4$  material decreased significantly, revealing higher separation efficiency of photo-excited charge and holes.

### 3.6. Photocatalytic tests

The photocatalytic performance of composites was mainly evaluated by photo-degradation of RhB. Blank experiment was carried out without any photocatalyst. The degradation efficiency was not changed, suggesting that the direct photolysis of RhB can be negligible under visible-light illumination. Fig. 9a presents efficiency for pure mpg- $C_3N_4$ , 0.1, 0.2, 0.5, 1, 2 and 3 wt% GQDs/mpg- $C_3N_4$

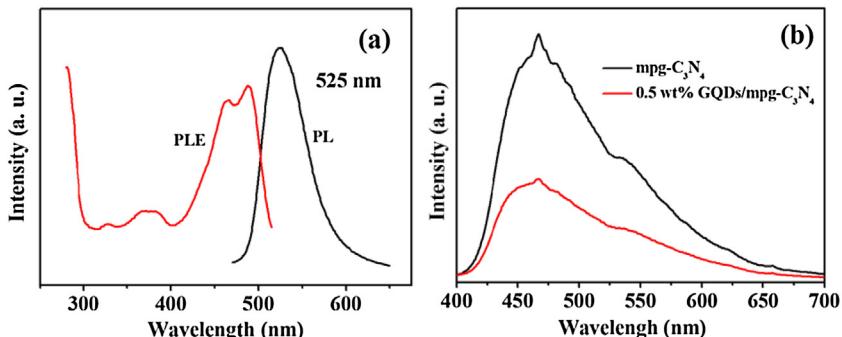


Fig. 8. PL and excitation (PLE) spectra of GQDs (a); photoluminescence spectra of pure mpg- $C_3N_4$  and 0.5 wt% GQDs/mpg- $C_3N_4$  (b).

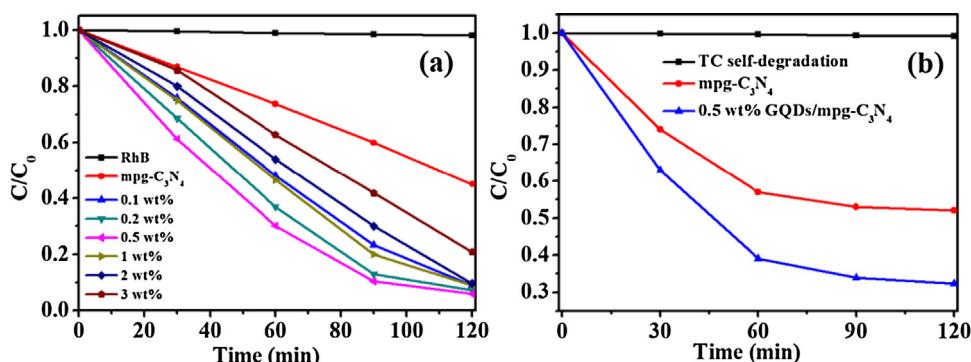
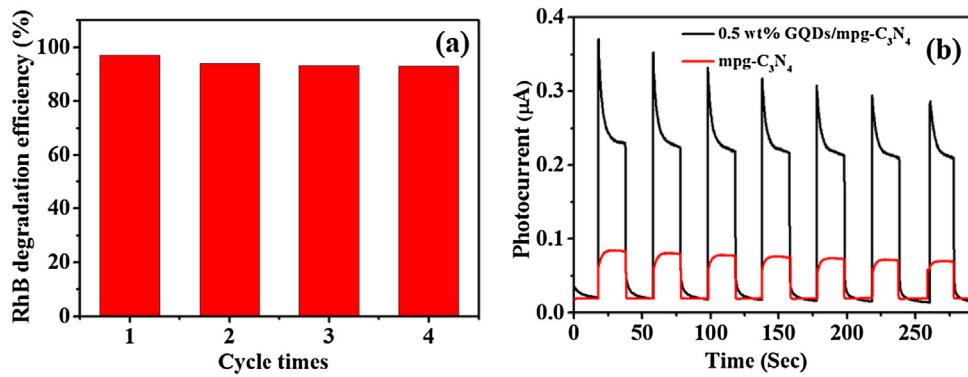
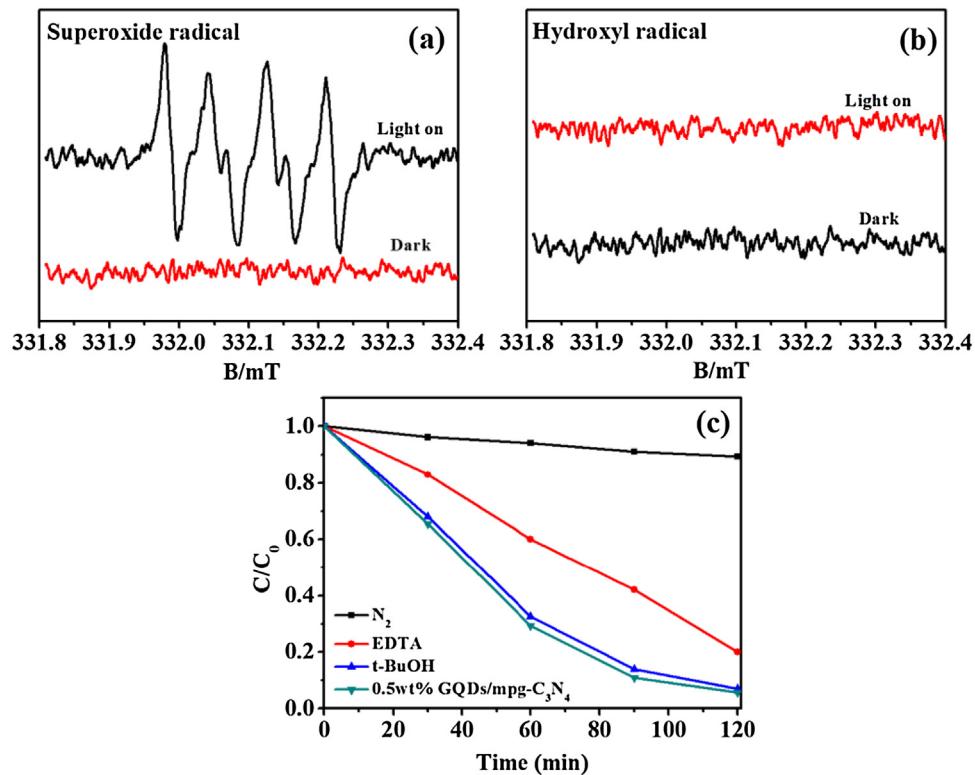


Fig. 9. Photocatalytic activity of RhB in the presence of the GQDs/mpg- $C_3N_4$  composites with different contents of GQDs under visible light irradiation (a); photocatalytic activity of TC in the presence of mpg- $C_3N_4$  and 0.5 wt% GQDs/mpg- $C_3N_4$  under visible light irradiation (b).



**Fig. 10.** Cycling runs for the photodegradation of RhB in the presence of 0.5 wt% GQDs/mpg-C<sub>3</sub>N<sub>4</sub> under visible light irradiation (a); transient photocurrent response of pure mpg-C<sub>3</sub>N<sub>4</sub> and 0.5 wt% GQDs/mpg-C<sub>3</sub>N<sub>4</sub> (b).



**Fig. 11.** ESR spectra of radical adducts trapped by DMPO: (a) DMPO-O<sub>2</sub><sup>−</sup> radical species of 0.5 wt% GQDs/mpg-C<sub>3</sub>N<sub>4</sub> was detected in methanol, (b) DMPO-OH was used to detect for 0.5 wt% GQDs/mpg-C<sub>3</sub>N<sub>4</sub> materials aqueous dispersion; (c) trapping experiment of active species during the photocatalytic degradation of RhB over 0.5 wt% GQDs/mpg-C<sub>3</sub>N<sub>4</sub> under visible light irradiation.

samples. As observed in Fig. 9a, the introduction of GQDs have an obviously influence on the photo-degradation efficiency. The 55% RhB could be removed by the pure mpg-C<sub>3</sub>N<sub>4</sub>, owing to unique mesoporous structure and moderate band gap. For 0.1 wt% GQDs/mpg-C<sub>3</sub>N<sub>4</sub> sample, the photocatalytic degradation efficiency was remarkably enhanced. During the GQDs content changed from 0.1 to 0.5 wt%, the photocatalytic activity was further increased. In comparison to the pure mpg-C<sub>3</sub>N<sub>4</sub>, 0.5 wt% GQDs/mpg-C<sub>3</sub>N<sub>4</sub> displayed the highest photocatalytic activity, which had a 42% improvement under visible-light illumination. A further increasing GQDs content caused a rapid reduction for the photocatalytic activity. Although the modification of GQDs were beneficial to charge transfer, too many GQDs cover on the surface of mpg-C<sub>3</sub>N<sub>4</sub> would limit the light absorption of mpg-C<sub>3</sub>N<sub>4</sub>. Therefore, the activity would decrease. To further investigate the photocatalytic degradation of colorless pollutions over GQDs/mpg-C<sub>3</sub>N<sub>4</sub> under visible light

irradiation, TC was chosen to evaluate the photocatalytic activity of GQDs/mpg-C<sub>3</sub>N<sub>4</sub> composites, and the results were shown in Fig. 9b. It was indicated that the 0.5 wt% GQDs/mpg-C<sub>3</sub>N<sub>4</sub> exhibited higher photocatalytic activity than that of pure mpg-C<sub>3</sub>N<sub>4</sub>. Therefore, it was implied that introduction of GQDs could effectively improve degradation performance of the composites. The stability and reusability of the composites are important factor from the viewpoint of practical applications, and the result is shown in Fig. 10a. After four cycles under uniform conditions, there was no apparent deactivation of the photocatalytic activity over 0.5 wt% GQDs/mpg-C<sub>3</sub>N<sub>4</sub>, indicating the high stability of 0.5 wt% GQDs/mpg-C<sub>3</sub>N<sub>4</sub>. The photocurrent tests were conducted for 0.5 wt% GQDs/mpg-C<sub>3</sub>N<sub>4</sub> and pure mpg-C<sub>3</sub>N<sub>4</sub> in a typical three electrode setup. In Fig. 10b, the higher photocurrent intensity obtained by GQDs/mpg-C<sub>3</sub>N<sub>4</sub> could be attributed to the modification of GQDs. The GQDs used as a co-catalyst, promoting the migration efficiency of photo-generated

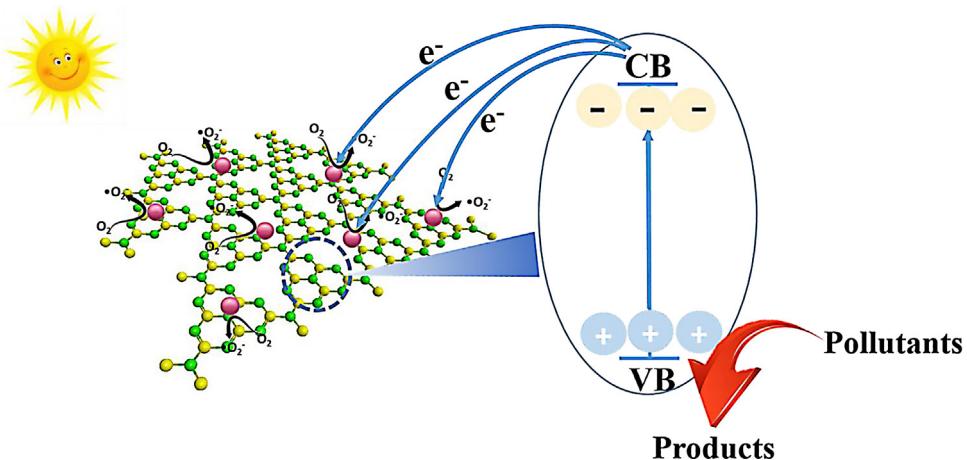


Fig. 12. Schematic model for the photocatalytic mechanism of GQDs/mpg-C<sub>3</sub>N<sub>4</sub> composites.

electrons. To sum up, the presence of synergistic effect between GQDs and mpg-C<sub>3</sub>N<sub>4</sub> facilitates the photo-generated electron from mpg-C<sub>3</sub>N<sub>4</sub> to GQDs, resulting in enhanced photocatalytic activity over GQDs/mpg-C<sub>3</sub>N<sub>4</sub>.

### 3.7. Possible reaction mechanism

In order to investigate the possible reactive species, ESR tests were used in the photoreaction process of GQDs/mpg-C<sub>3</sub>N<sub>4</sub> with DMPO in water solution. In Fig. 11a, the GQDs/mpg-C<sub>3</sub>N<sub>4</sub> composites were irradiated for 12 min and successfully detected the DMPO-O<sub>2</sub><sup>·-</sup> species in media solution. The results indicated that O<sub>2</sub><sup>·-</sup> was main reactive species under visible light illumination, while no signals were detected without light illumination. As shown in Fig. 11b, no signals of ·OH were detected whatever under visible light irradiation or in the dark. Therefore, ·OH was not main species in GQDs/mpg-C<sub>3</sub>N<sub>4</sub> photocatalytic reaction system.

To further reveal the roles of the main active species on the photoreaction process over GQDs/mpg-C<sub>3</sub>N<sub>4</sub> composites, free radicals trapping experiments were tested, and the results were shown in Fig. 11c. The t-BuOH was used as hydroxyl radical scavenger and EDTA-2Na as holes scavenger. Purging N<sub>2</sub> into the solution could make an anaerobic environment, which would prohibit the formation of superoxide radical (·O<sub>2</sub><sup>·-</sup>) [74]. The photocatalytic activity of GQDs/mpg-C<sub>3</sub>N<sub>4</sub> was slightly inhibited after addition of EDTA-2Na as the holes scavenger, suggesting that holes as active species also taken part in the photodegradation process. When the t-BuOH as electronic quenching agent was added, the photodegradation efficiency of RhB did not obviously reduced, which imply that the ·OH was not the main free radicals species. Therefore, the ESR investigation and trapping experiment indicated that ·O<sub>2</sub><sup>·-</sup> was active species for this photocatalytic system.

Based on above trapping experiment and ESR results, the possible mechanism schematic of 0.5 wt% GQDs/mpg-C<sub>3</sub>N<sub>4</sub> system is presented in Fig. 12. When mpg-C<sub>3</sub>N<sub>4</sub> was irradiated under visible light illumination, only a small part of photo-generated electrons participated in photocatalytic reaction process, and the other photo-generated electrons could recombine with holes rapidly. However, in GQDs/mpg-C<sub>3</sub>N<sub>4</sub> system, the recombine rate between photo-generated electron and holes was greatly inhibited due to the role of GQDs. The photo-generated electrons from CB of mpg-C<sub>3</sub>N<sub>4</sub> sheets could be transferred to GQDs surface quickly, and then generated superoxide. Therefore, the photocatalytic activity was improved.

## 4. Conclusions

In summary, GQDs/mpg-C<sub>3</sub>N<sub>4</sub> composites were prepared utilizing electrostatic attraction. The effects of GQDs contents on the photo-degradation efficiency of RhB dye were investigated. The maximum removal efficiency of RhB reached 97% by using 0.5 wt% GQDs/mpg-C<sub>3</sub>N<sub>4</sub> under visible light illumination. Meanwhile, the composites could effectively remove the colorless organic pollutants TC. The high photocatalytic activity of composites was attributed to the introduction of GQDs as electron acceptor. According to the ESR investigation and trapping experiment, ·O<sub>2</sub><sup>·-</sup> was the main active species for photo-degradation of pollutants.

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